

Origins of elastic properties in ordered nanocomposites

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We predict a diblock copolymer melt in the lamellar phase with added spherical nanoparticles that have an affinity for one block to have a *lower* tensile modulus than a pure diblock copolymer system. This weakening is due to the swelling of the lamellar domain by nanoparticles and the displacement of polymer by elastically inert fillers. Despite the overall decrease in the tensile modulus of a polydomain sample, the shear modulus for a single domain increases dramatically.

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Polymer nanocomposites are being extensively investigated because of the improvement in material properties that result from the addition of nanoscopic filler particles to the polymer matrix [1, 2, 3, 4]. In addition to their practical importance, such composites offer diverse scientific challenges, combining ideas from colloid science, polymer physics and chemistry, as well as material science. Polymer nanocomposites become even more interesting when the polymer matrix consists of a block copolymer, capable of self-assembling into a wide range of ordered nanoscaled structures — nanoparticles can then be sequestered in certain domains to form ordered nanocomposites [5, 6, 7, 8]. The simultaneous amphiphilic and colloidal self-assembly taking place in such ordered nanocomposites gives them complex structures [9] and makes the structure-property relationship particularly intriguing. Since there is little understanding of the mechanical properties that arise in ordered nanocomposites, we present in this theoretical work a first investigation of the *origins* of the elastic properties of an ordered nanocomposite with spherical nanofillers.

Buxton and Balazs [10] have studied a phenomenological model of nanosphere filled block copolymer systems in which a hybrid Cahn-Hilliard/Brownian dynamics simulation is used as input to a lattice spring model of the elastic moduli. Their approach provides a versatile and useful method of predicting properties, but lacks polymeric detail in the elasticity portion of the simulation. Furthermore, they examine filled block copolymer systems in the solid state, where all morphological evolution is disregarded as the system is distorted.

We examine the elastic properties of a melt state ordered nanocomposite using self-consistent field theory (SCFT). SCFT is a coarse-grained, first principles approach that been successful in dealing with block copolymer structure [11]. In the framework of this theory, local monomer density profiles of different block copolymer chemical species are represented self-consistently using chemical potential fields. Both the densities and the fields are then used to determine the free energy for the system, and if desired, the internal energies and entropies can be explicitly calculated. SCFT has been extended to

deal with hard nanosphere/block copolymer nanocomposites by the incorporation of a density functional theory particle contribution [12, 13]. Further, Tyler and Morse have demonstrated that the linear elastic behavior of a melt block copolymer system, which is quasi-statically deformed can be well characterized using SCFT [14]. We have recently adapted this approach to an efficient real space, pseudo-spectral method [15] and found an increasing elastic modulus in multiblock copolymer systems as a function of block number, in qualitative agreement with experiment [16]. Here, we combine these two advances in order not only to predict the effect on the elastic properties of adding nanoparticles to a block copolymer melt, but also to explain the *physical origins* of the observed effects.

We will study the prototypical system consisting of a symmetric AB diblock copolymer melt in the lamellar phase with added spherical nanoparticles that have an affinity for the A block of the copolymer. Consequently, a lamellar morphology with the particles sequestered in the A phase is being considered, and the system's tetragonal symmetry is elastically characterized by just five independent non-zero components of the elastic modulus tensor. Additionally, the system is in a melt state so that deformations parallel to the lamellar structure have no effect on the free energy of the system [15]. We are thus left with only two relevant moduli, K_{33} and K_{44} . Therefore we deform the system quasi-statically in two ways; it is subjected to an extension/compression, and to a simple shear. These deformations allow us to determine the K_{33} and K_{44} components of the elastic modulus tensor [17], corresponding to extension/compression and shear moduli, respectively. These components are found by taking the second derivative of the SCFT free energy with respect to the relative deformation. Greater detail on the methodology can be found in Ref. [15].

We chose a system with a segregation of $\chi N = 25$ between the A and B blocks, with the particles considered to be of the A species. χ is the Flory-Huggins monomer segregation parameter and N is the degree of polymerization of the entire diblock. The particles radius was chosen to be $0.725R_g$, where R_g is the unperturbed radius

modulus	0%	15%	Δ modulus
K_{33}	4.67	3.40	1.27
K_{33}^U	2.75	2.03	0.72
K_{33}^{ST}	-0.58	-0.56	-0.02
K_{33}^{SA}	1.25	0.36	0.89
K_{33}^{SB}	1.25	1.39	-0.13
$K_{33}^{S_{id}}$	0.0	0.22	-0.22
$K_{33}^{S_{st}}$	0.0	-0.04	0.04

TABLE I: Components of the K_{33} elastic modulus for 0% and 15% added nanoparticles. The change in the modulus between the pure diblock and the filled diblock system is recorded in the last column.

modulus	0%	15%	Δ modulus
K_{44}	0.01	0.05	-0.04
K_{44}^U	1.10	0.94	0.16
K_{44}^{ST}	-0.53	-0.51	-0.02
K_{44}^{SA}	-0.28	-0.22	-0.06
K_{44}^{SB}	-0.29	-0.07	-0.22
$K_{44}^{S_{id}}$	0.0	-0.02	0.02
$K_{44}^{S_{st}}$	0.0	-0.07	0.07

TABLE II: Components of the K_{44} elastic modulus for 0% and 15% added nanoparticles. The change in modulus between the pure diblock and the filled diblock system is recorded in the last column.

of gyration of a diblock molecule. Finally, the particle-to-diblock volume ratio was ~ 3.6 , and a 15% volume fraction of spherical fillers was added. The system was deformed in the two ways described above and compared with a neat diblock system similarly deformed. The K_{33} and K_{44} moduli in each case were used to find a tensile modulus by averaging over a polydomain sample according to the Hill prescription [18] as described in Ref. [15].

For the pure diblock system a dimensionless tensile modulus of ~ 0.4 was found while for the nanocomposite system, the modulus was ~ 0.3 . Thus we predict that the addition of nanoparticles will *weaken* the material. Normally, one expects the addition of nanofillers to strengthen the composite, rather than weaken it [2], although a reduced modulus has been observed experimentally in exfoliated layered silicate/triblock nanocomposites [5]. The reduced modulus found for our present system can be explained by decomposing the K_{33} and K_{44} moduli as shown in tables I and II. These tables show total K_{33} and K_{44} moduli values, respectively, for 0% and 15% added fillers, as well as the difference between the filled and unfilled system moduli. The tables also give the contributions to the moduli of the internal energy (U), translational entropy (S_T), and the A and B conformational entropies of the diblocks (S_A and S_B). Also listed are the ideal gas (S_{id}) and steric (S_{st}) contributions of the filler particles. For information on how

these components are calculated, see Ref. [15]. Comparing the total K_{33} and K_{44} , it is observed that the main contribution to the tensile modulus arises from the extensional modulus K_{33} . Furthermore, the main drop in K_{33} from the 0% to the 15% case is a result of the internal energy contribution and the A block conformational entropy contribution.

These two contributions can be examined separately. Upon extension/compression, SCFT shows that the lamellar interfacial width remains practically unchanged in both the filled and unfilled cases. Furthermore, the A and B domains are well segregated both before and after deformation, indicating that there are few A monomers in the B region and *vice versa*. Thus the absolute amount of energetically unfavorable AB contacts is the same before and after deformation, whereas the domain size changes. Adapting an expression of Matsen and Bates [19], the internal energy contribution to the free energy is

$$\frac{U}{k_B T} \propto \frac{1}{V} \int d\mathbf{r} [\varphi_A(\mathbf{r}) + \varphi_p(\mathbf{r})] \varphi_B(\mathbf{r}) \quad (1)$$

where T is the temperature and k_B is Boltzmann's constant. $\varphi_A(\mathbf{r})$, $\varphi_B(\mathbf{r})$ and $\varphi_p(\mathbf{r})$ are the local volume fractions of A and B monomers, and particles, respectively. The integral in Eq. (1) is constant under the conditions described above, so that the internal energy is inversely proportional to the volume. The lamellar morphology is one dimensional, so that the internal energy can be written as inversely proportional to the equilibrium domain size d^* .

$$\frac{U}{k_B T} = \frac{\alpha}{d^*} \quad (2)$$

where α is a constant. A relative deformation ϵ that leaves the interfacial width and the bulk mixing unchanged, changes Eq. (2) into

$$\frac{U}{k_B T} = \frac{\alpha}{d^*(1 + \epsilon)}. \quad (3)$$

The SCFT internal energy for extensions/compressions is shown in Fig. 1(a). Both for pure diblock and for filled systems, the behavior reflected in Eq. (3) is observed. An estimate of the modulus K_{33}^U can be found by taking the second derivative of Eq. (3) with respect to the relative deformation, which gives

$$K_{33}^U = \left. \frac{d^2(U/k_B T)}{d\epsilon^2} \right|_{\epsilon=0} = \frac{2\alpha}{d^*} \quad (4)$$

showing that the U contribution to the K_{33} modulus is also inversely proportional to the equilibrium spacing. SCFT shows that the addition of filler particles enlarges the equilibrium domain size of the nanocomposite compared to the pure diblock system. Equation (4) then indicates that the modulus will drop, as observed. In other words, the modulus is weakened partially because

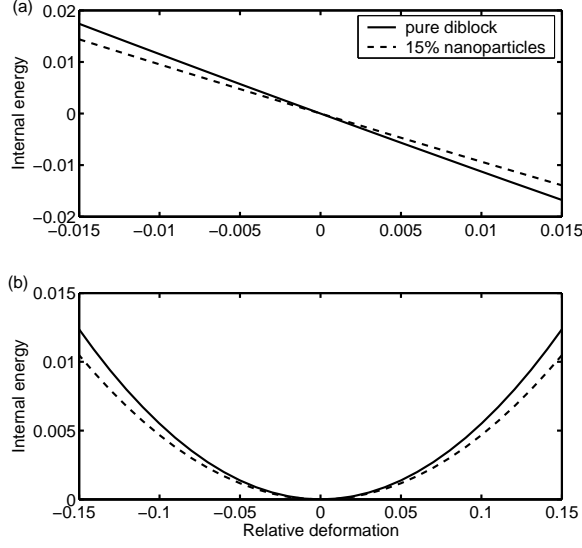


FIG. 1: Internal energy contribution to the free energy versus relative distortion for extension/compression (a) and shear (b) of a diblock system. The neat diblock free energy is plotted with the solid line whereas the 15% filled system is shown with dashed line. In (a), negative deformations are compressions while positive deformations are extensions. In all plots, energies have been zeroed around the equilibrium spacing, which is represented by $\epsilon = 0$.

there is less interface per volume in the nanocomposite compared to the pure diblock.

The A block configurational entropy also contributes to the overall drop in modulus. The filler particles have no configurational entropy; in the filled system the S_A energy portion will rise (drop) under extension (compression) at a slower rate because there is a smaller fraction of chains to stretch (relax). This can be seen in Fig. 2(a). Thus filler particles weaken the material because they displace polymers that have stretching energy, which could contribute positively to the elastic modulus. In other words, the modulus is weakened partially because there is less polymer and more elastically inert filler per volume.

As mentioned, the shear modulus K_{44} only makes a small contribution to the tensile modulus, but it is interesting to examine it nonetheless. Table II shows that while the K_{33} modulus drops upon the addition of fillers, K_{44} increases by more than 400%. From table II, this increase can be seen to be due to a very large increase in the B block conformational entropy contribution to the modulus. This is partially reduced by a drop in the internal energy contribution, but is still very large.

As in the extension/compression case, the interfacial profiles do not change significantly upon shearing of the sample. The consequence is that the internal energy again is inversely proportional to the volume of the system, as previously explained. The B block conforma-

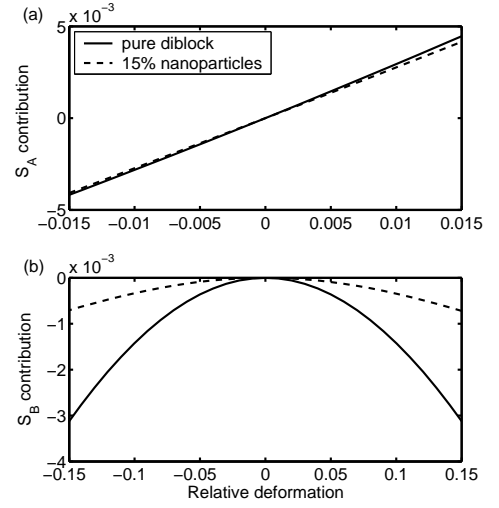


FIG. 2: Conformational entropy contribution to the free energy versus distortion for extension/compression (a) and shear (b) of a diblock system. The neat diblock free energy is plotted with the solid lines whereas the 15% filled system is shown with dashed lines. In (a), negative deformations are compressions while positive deformations are extensions; the S_A contribution is shown in (a). The S_B contribution is shown in (b). In all plots, energies have been zeroed around the equilibrium spacing, which is represented by $\epsilon = 0$.

tional entropy contribution to the free energy behaves similarly; from Matsen and Bates [19], the B block energy is

$$\frac{-S_B}{k_B} \propto -\frac{1}{V} \int d\mathbf{r} \{ \rho_J(\mathbf{r}) \ln q^\dagger(\mathbf{r}, f) + w_B(\mathbf{r}) \varphi_B(\mathbf{r}) \} \quad (5)$$

where $\rho_J(\mathbf{r})$ is the distribution of diblock junction points, $w_B(\mathbf{r})$ is the chemical potential field for the B monomer distribution, and $q^\dagger(\mathbf{r}, s)$ is a SCFT propagator. A detailed explanation of Eq. (5) can be found elsewhere [11, 19]. If we for the moment ignore the contribution of the integral in Eq. (5), the B conformational contribution can be written as

$$\frac{-S_B}{k_B} = -\frac{\beta}{V \sin \theta} \quad (6)$$

where β is a constant. A $\sin \theta$ has been added to the denominator of Eq. (6) to account for the effect of a shear change in volume. When the sample is sheared, the volume is reduced; θ is a measure of the amount of shear with $\theta = \pi/2$ representing a non-sheared system. See Ref. [15] for more explanations. The internal energy (2) will be similarly affected. From Ref. [15], the shear angle is related to the relative distortion through $\epsilon = \cot \theta$. The internal energy and B conformational entropy are then

$$\frac{U}{k_B T} = \frac{\alpha}{V} \sqrt{\epsilon^2 + 1}, \quad (7)$$

$$\frac{-S_B}{k_B} = -\frac{\beta}{V}\sqrt{\epsilon^2 + 1}. \quad (8)$$

Figures 1(b) and 2(b) show that the internal energy and B block contribution to the free energy obey the relationships (7) and (8), respectively, for both the filled and unfilled systems. The moduli for these are found through the second derivative with respect to ϵ and are

$$K_{44}^U = \frac{\alpha}{V}, \quad (9)$$

$$K_{44}^{S_B} = -\frac{\beta}{V}. \quad (10)$$

Both K_{44}^U and $K_{44}^{S_B}$ are inversely proportional to the equilibrium volume, with the important difference of a minus sign. Thus as the equilibrium volume is enlarged upon the addition of fillers, the S_B contribution to the modulus becomes a smaller *negative* number, so the material is *stronger*. This effect is somewhat reduced as the U contribution to the modulus will become smaller for the larger equilibrium volume of the filled system. In other words, diblock molecules' entropies want to help shear the system (see Fig. 2(b)). The larger domain size of the filled system means that there is less stretching energy per volume (see eq. (8)), the molecules are more relaxed to begin with at equilibrium, and so are less inclined to help deform the system, which makes the material stronger. This effect is reduced since there is less interface per volume in the filled system. The A block is not treated the same way, since with the fillers added the S_A contribution to the free energy cannot be written in a form such as Eq.(6).

In summary, we have calculated the tensile modulus for a neat diblock copolymer system and for a diblock nanocomposite with 15% added nanospheres. Both systems were considered to be in the lamellar phase, and deformations were applied quasi-statically. The elastic modulus tensor components K_{33} and K_{44} were found and used to derive a tensile modulus for a polydomain sample. It was found that the addition of nanoparticles *weakened* the material. This was attributed to the larger lamellar domain size of the equilibrium filled system — it had less interface per volume — and to the displacement of polymer by the filler particles — there was less elastic polymer per volume. Although, the shear modulus contributed little, it was acted on by similar mechanisms, with the result that it *increased* dramatically upon the addition of nanofillers. Given that ordered nanocomposites of the sort described here can now be realized, we believe our predictions should be amenable to experimental verification. It would be interesting to change the distribution of the particles in the block copolymer through changes of wetting properties, particle size, or volume fraction.

Such changes in structure could significantly change the properties.

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